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(71) Applicant: **BAUSCH & LOMB INCORPORATED**
Rochester, New York 14604-2701 (US)

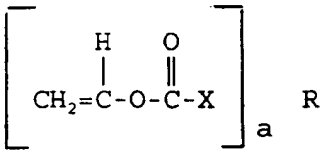
(72) Inventors:
- **Bambury, Ronald E.**
  Fairport, New York 14450 (US)
- **Seelye, David E.**
  Rochester, New York 14624 (US)

(74) Representative: **Allam, Peter Clerk**
LLOYD WISE, TREGEAR & CO.,
Commonwealth House,
1-19 New Oxford Street
London WC1A 1LW (GB)

Remarks:
This application was filed on 24 - 10 - 1996 as a divisional application to the application mentioned under INID code 62.

(54) Vinyl carbonate and vinyl carbamate monomers for a contact lens material

(57) There is provided a compound of the general formula:



wherein

a is 1, 2, 3 or 4;

X is -O-, -S- or -NR^3-;

R^3 is H or a monovalent alkyl radical; and

R is selected from an organosilicon radical, a heterocyclic-containing radical, an adamantyl-containing radical, an alkylene radical, a fluoroalkylene radical and a hydroxyalkyl radical.

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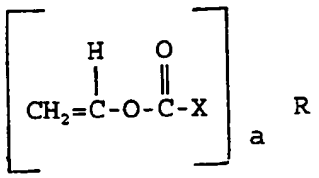
Description

This invention relates to novel compounds which are useful in the manufacture of copolymers from which biomedical materials, and especially contact lenses, can be fabricated. The application has been divided out of our European Patent Application No. 90304659.7 (Publication No. EP-A-0396364).

The parent application describes and claims novel copolymers, and contact lenses fabricated therefrom, formed by polymerizing a prepolymer mixture comprising:

(a) a compound of the general formula (I):



(I)

wherein

a is 1, 2, 3 or 4;

X is -O-, -S- or -NR^3-;

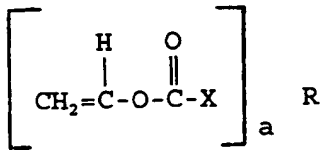
R^3 is H or a monovalent alkyl radical; and

R is selected from an organosilicon radical, a cycloalkyl-containing radical, a cycloaryl-containing radical, a heterocyclic-containing radical, an alkylene radical, an oxyalkylene radical, a fluoroalkylene radical, a haloalkyl radical and a hydroxyalkyl radical; and

(b) a crosslinking agent.

The present invention is concerned with certain compounds, within the scope of formula (I) above, which are novel per se.

The compounds of the present invention have the general formula (II):



(II)

wherein

a is 1, 2, 3 or 4;

X is -O-, -S- or -NR^3-;

R^3 is H or a monovalent alkyl radical; and

R is selected from an organosilicon radical, a heterocyclic-containing radical, an adamantyl-containing radical, an alkylene radical, a fluoroalkylene radical and a hydroxyalkyl radical.

The compounds of the present invention are useful in the manufacture of the copolymers to which the parent application relates and can serve either as the monomers of component (a) of the prepolymer mixture or, in some cases, as the crosslinking agent component (b) of the prepolymer mixture.

The monomers of this invention generally fall into the following classifications, viz:

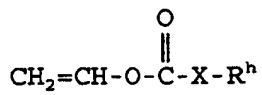
(a) hydrophilic monomers, wherein the R moiety is hydrophilic so that the monomer as a whole is relatively hydrophilic, and

(b) non- or slightly hydrophilic monomers wherein the R moiety is non-hydrophilic.

The properties of the resulting copolymers, and therefore of contact lenses made from the copolymers, vary depending on the nature of the R moiety, as is more fully explained in the parent specification. Some examples of the three types of R moiety mentioned above will now be described.

HYDROPHILIC MONOMERS

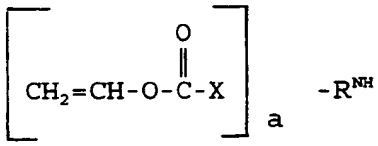
The hydrophilic monomers of this invention represented by the general formula:



where X is as previously defined and R^h denotes a hydrophilic moiety within the definition of R given hereinbefore. Examples of hydrophilic monomers of this invention include 2-hydroxyethyl vinyl carbonate, 2-hydroxyethyl vinyl carbamate, 3-(2-pyrrolidinon-1-yl)propyl vinyl carbonate, 2-(2-pyrrolidinon-1-yl)ethyl vinyl carbonate, N-(vinyloxycarbonyloxy)pyrrolidin-2,5-dione, N-[vinyloxycarbonyloxyethyl]pyrrolidin-2,5-dione, N,N-dimethyl vinyl carbamate and N,N-diethyl vinyl carbamate.

NON-HYDROPHILIC MONOMERS

The non- or slightly hydrophilic monomers of this invention may be represented by the following general formula:

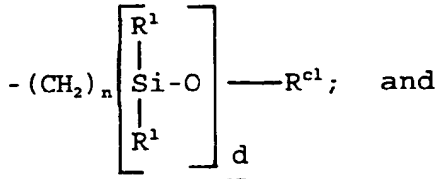


where X and a are as previously defined and R^{NH} denotes a non-hydrophilic moiety within the definition of R given hereinbefore.

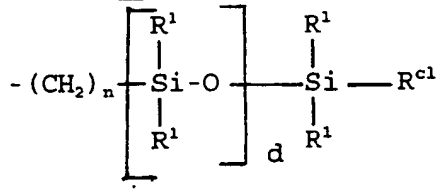
In certain embodiments of the invention, R^{NH} may be described by the following formulae:

$$-(CH_2)n[Si(CH_2)_mCH_3]_3;$$

$$-(CH_2)n\ Si(OSi[(CH_2)_mCH_3]_3)_3;$$

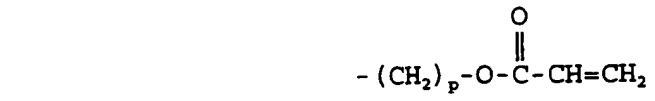


and



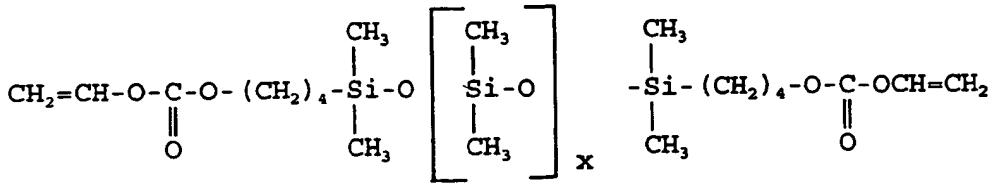
where R^1 denotes a monovalent organic radical such as an alkyl radical with 1 to 6 carbon atoms, or a fluoroalkyl radical with 1 to 6 carbon atoms;

R^{cl} denotes



p is 1 to 6; and
d is 1-200, and
where n is 1, 2, 3 or 4, m is 0, 1, 2, 3, 4 or 5, or R^{NH} denotes a partially or fully fluorinated alkyl, alkylaryl or aryl radical.

The non-hydrophilic monomers specifically include t-butyldimethylsiloxyethyl vinyl carbonate; 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbonate; 1,3-bis[4-(vinyloxycarbonyloxy)but-1-yl]tetramethyldisiloxane; 3-(trimethylsilyl)propyl vinyl carbonate; t-butyldimethylsiloxyethyl vinyl carbonate; trimethylsilylmethyl vinyl carbonate; trimethylsilylethyl vinyl carbonate; 2,2,2-trifluoroethyl vinyl carbonate; t-butyl vinyl carbonate; 3-[tris(trimethylsiloxy)silyl] propyl vinyl carbonate; 3-(vinyloxycarbonylthio)propyl-[tris(trimethylsiloxy)silane]; 3-[tris-(trimethylsiloxy)silyl]propyl vinyl carbamate; and



where X = 25 on the average (so-called "V_2D_{25}" monomers).

The preferred non-hydrophilic monomers for use in preparing the copolymers of the parent application are the long chain siloxane monomers such as the so-called "V_2D_{25}" monomers referred to above.

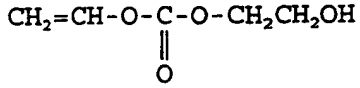
As is taught in the parent application, some of the compounds of this invention are also useful as the crosslinking agents in the prepolymer mixtures from which the biomedically useful copolymers are formed.

The invention is illustrated by the Examples which follow.

PART I - SYNTHESIS OF HYDROXALKYL MONOMERS

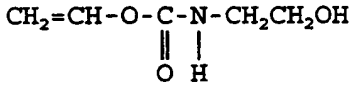
1.0 2-Hydroxyethyl Vinyl Carbonate $C_6H_8O_4$

To a 1000 mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, N_2 blanket, thermometer, and a dropping funnel 5.0 g (81.66 mmol) of ethylene glycol 7.12 g (90.0 mmol) of pyridine and 500 mL of chloroform were added. To this reaction mixture 8.77 g (81.66 mmol) of vinyl chloroformate was added over 20 minutes. The reaction mixture was stirred for 16 hours. The volume of the mixture was reduced to 75 mL on a rotary evaporator and the residue washed with 100 mL of 2N HCl. The aqueous phase was set aside. The organic phase was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil was purified by chromatography (silica gel, gradient starting with 60% cyclohexane 40% chloroform) to give an oil. The 2N HCl wash was saturated with sodium chloride and extracted three times with 50 mL chloroform. The combined chloroform extracts were dried with magnesium sulfate and flash evaporated to an oil. The oils combined to give 2.3 g (17.4 mmol, 21.3%) of a light yellow oil. FTIR (neat, capillary) 3500.56, 33477.38, 3379.94, 2960.20, 1805.29, 1753.69, 1650.79, 1558.65, 1540.44, 1506.71, 1481.33, 1455.89, 1388.72, 1373.25, 1299.19, 1244.25, 1154.19, 1067.30, 1015.59, 995.52, 969.77, 944.14, 913.44, 875.08, 859.65, 779.15, 717.53, 684.06, 666.45, 649.43. NMR ($CDCL_3$) δ 6.83-7.177 (1H,m), 4.56-5.0 (2H,m), 3.70-3.93 (2H,m), 3.07-3.43 (1H,s). The instrumental analyses were consistent with a compound represented by the following formula:



1.1 2-Hydroxyethyl Vinyl Carbamate $C_5H_9NO_3$

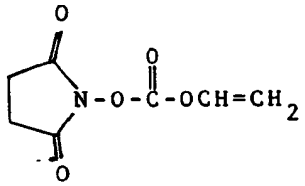
To a 500 mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, N_2 blanket, thermometer, and dropping funnel 20.0 g (327.4 mmol) of ethanolamine and 200 mL of chloroform were added. 17.44 g (163.7 mmol) of vinyl chloroformate was added to the mixture over 20 minutes raising the temperature to 53°C. The reaction mixture was cooled to room temperature and stirred for 16 hours. The resolution precipitate was removed by filtration. The filtrate was evaporated to remove solvent and the residual oil was distilled (125°C ± 5°C, .89 Torr) to give 21.2 g (161.7 mmol, 98.8%) of a light yellow oil. FTIR (neat, capillary) 3314.69, 2940.08, 2885.15, 1705.86, 1648.26, 1522.62, 1458.28, 1432.05, 1403.96, 1363.49, 1339.67, 1294.21, 1244.90, 1160.44, 1116.66, 1059.67, 1010.44, 947.03, 921.01, 861.00, 768.57, 731.09, NMR ($CDCL_3$) δ 6.90-7.23 (1H,m), 5.76-6.3 (1H,s), 4.26-4.83 (2H,m), 3.50-3.93 (3H,m), 3.07-3.47 (2H,m). The spectral analyses were consistent with the following chemical structure:



PART II - SYNTHESIS OF PYRROLIDINONE MOIETY CONTAINING MONOMERS

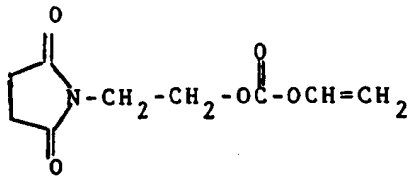
2.0 N-(Vinyloxycarbonyloxy)-pyrrolidin-2,5-dione

To a 500 mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, dropping funnel, ice-saltwater bath, and thermometer were added 10.0 (87.0 mmol) of N-hydroxy succinimide, 6.9 g (87.0 mmol) of pyridine, and 100 mL tetrahydrofuran was added. To the reaction mixture 9.25 g (87.0 mmol) of vinyl chloroformate was added so that the temperature remained below 10°C. After stirring at room temperature for 18 hours the reaction mixture was washed with 100 mL HCl, and 100 mL 2N NaOH. The organic phase was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting liquid chromatographed (silica gel, chloroform) to yield 10.0 g (54.0 mmol, 62.1% yield) of an oil. FTIR (neat, capillary) 3516.50, 3132.04, 3099.40, 3003.94, 2960.21, 18330.80, 1823.25, 1792.36, 1734.05, 1671.98, 1653.62, 1646.30, 1429.97, 1380.77, 1368.60, 1306.35, 1260.89, 1241.83, 1201.12, 1162.09, 1154.49, 1134.29, 1087.59, 1049.93, 1005.21, 990.18, 948.77, 941.86, 908.06, 897.29, 892.42, 812.37, 769.04, 756.85, 724.90, 707.81. NMR ($CDCl_3$) 6.73-7.09 (1H,q), 4.61-5.24 (2H,m), 2.78 (4H,S).



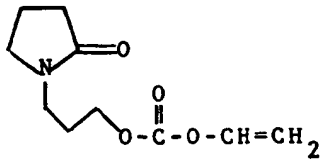
2.1 N-(Vinyloxycarbonyloxyethyl)pyrrolidone-2,5-dione

To a 500 mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, dropping funnel, ice-saltwater bath, and thermometer were added 5.0 (35.0 mmol) of N-(2-hydroxyethyl) succinimide, 2.8 g (35.0 mmol) of pyridine, and 100 mL chloroform. To the reaction mixture was added 3.7 g (35.0 mmol) of vinyl chloroformate so that the temperature remained below 10°C. After stirring at room temperature for 18 hours the reaction mixture was washed with 100 mL 2N HCl and 100 mL 2N NaOH. The organic phase was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting red liquid chromatographed (silica gel, chloroform). The recovered oil totalled 3.0 g (14.1 mmol, 40.2% yield). FTIR (neat, capillary) 1755.10, 1694.90, 1648.77, 1427.00, 1396.38, 1366.15, 1329.97, 1298.34, 1239.58, 1185.85, 1152.26, 1111.20, 1085.92, 1024.25, 1005.00, 946.53, 894.87, 882.46, 848.52, 818.51, 778.99, 700.00, 661.32. NMR ($CDCl_3$) 6.50-6.83 (1H,q), 4.13-4.66 (2H,m), 3.93-4.13 (2H,m), 3.33-3.66 (2H,m), 2.41 (4H,S).



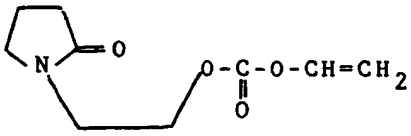
2.2 3-(2-Pyrrolidinon-1-yl)propyl Vinyl Carbonate $C_{10}H_5NO_4$

To a 250 mL 1-neck round bottom flask fitted with a magnetic stirrer, dropping funnel, and ice bath, 12.5 g (87.3 mmol) of N-(3-hydroxypropyl)-2-pyrrolidinone, 7.6 g (96.0 mmol) of pyridine and 100 mL of chloroform were added. To the ice cold reaction mixture 9.3 g (87.3 mmol) of vinyl chloroformate was added over 5 minutes. After 5 minutes a precipitate formed. The reaction mixture was adsorbed on silica gel then purified by chromatography (silica gel, methylene chloride) to give 17.3 g (81.1 mmol, 93.0%) of a straw coloured oil. FTIR (neat, capillary) 2963.22, 1754.09, 1676.89, 1646.83, 1566.02, 1494.64, 1463.44, 1425.05, 1396.11, 1357.91, 1336.92, 1296.25, 1239.43, 1152.41, 1085.28, 1024.06, 998.00, 946.11, 882.00, 761.74, 737.53, 697.39, 651.25. NMR ($CDCl_3$) 6.82-7.17 (1H,m), 4.40-4.96 (2H,m), 4.06-4.28 (2H,m), 3.24-3.47 (4H,m), 1.68-2.56 (6H,m). The spectral analyses were consistent with the following chemical structure:



2.3 2-(2-Pyrrolidinon-1-yl)ethyl Vinyl Carbonate $C_9H_{13}NO_3$

To a 250 mL 1-neck round bottom flask fitted with a magnetic stirrer, dropping funnel, and ice bath, were added 10.0 g (77.4 mmol) of N-2-(hydroxyethyl) pyrrolidinone, 6.7 g (84.7 mmol) of pyridine and 100 mL of chloroform. To the ice cold solution 8.3 g (78.0 mmol) of vinyl chloroformate was added. The mixture was stirred for 30 minutes, forming a precipitate. The reaction mixture was chromatographed (silica gel, methylene chloride) 90% toluene 10%) to give 8.3 g (41.7 mmol, 53.9% of a light yellow oil. FTIR (neat, capillary) 2962.91, 1754.66, 1679.48, 1646.22, 1494.64, 1462.88, 1438.22, 1424.48, 1393.77, 1368.15, 1327.55, 1286.44, 1237.47, 1152.71, 1113.47, 1085.63, 1046.25, 1018.86, 979.70, 946.17, 894.98, 877.43, 853.32, 779.37, 735.01, 697.06, 650.86. NMR ($CDCl_3$) δ 6.84-7.17 (1H,m), 4.45-5.01 (2H,m), 4.18-4.35 (2H,m), 3.32-3.62 (4H,m), 1.70-2.50 (4H,m). Spectral analyses were consistent with the proposed chemical structure.

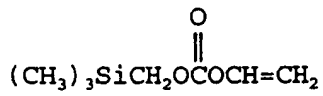


PART III - SILICON CONTAINING MONOMERS

3.0 Trimethylsilylmethyl Vinyl Carbonate $C_7H_{14}O_3Si$

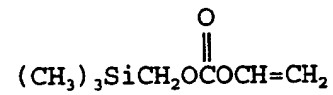
To a 250 mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, dropping funnel,

and thermometer was added 3.8 g (48.0 mmol) of pyridine then 50 mL of chloroform. The mixture was cooled to 12°C ± 3°C with an ice-water bath. Next 5.0 g (48.0 mmol) of trimethylsilyl methanol then 5.1 g (48.0 mmol) of vinyl chloroformate were slowly added so that the temperature was maintained. The cooling bath was removed and the reaction mixture was stirred for one hour. The organics were washed four times with 100 mL 2N HCl, twice with distilled water and then dried over magnesium sulfate. The solvent was removed under reduced pressure to give an oil. The oil was passed through silica gel to give 4.8 g (27.56 mmol, 57.1%) of colourless oil. FTIR (neat, capillary) 2958.37, 1754.67, 1648.09, 1420.24, 1383.80, 1302.02, 1226.95, 1155.20, 1085.49, 944.10, 913.47, 840.69, 779.53, 735.76, 669.81, 668.88. NMR ($CDCl_3$) δ 6.73-7.07 (1H,m), 4.25-4.85 (2H,m), 3.73 (2H,S), 0.00 (9H,S).



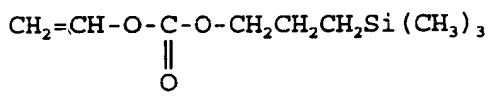
3.1 Trimethylsilylethyl Vinyl Carbonate $C_8H_{16}O_3Si$

To a 250 mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, dropping funnel, and thermometer was added 6.69 g (85.0 mmol) of pyridine then 100 mL of chloroform. The reaction was cooled to 12°C ± 3°C with an ice-water bath. Next 10.0 g (85.0 mmol) of trimethylsilyl ethanol and 9.01 g (85.0 mmol) of vinyl chloroformate were added so that the temperature was maintained. The cooling bath was removed and the reaction mixture was stirred for one hour. The organic phase was washed four times with 100 mL 2N HCl, twice with distilled water then dried over magnesium sulfate. The solvent was removed under reduced pressure to give an oil. The oil was passed through silica gel to give 6.0 g (31.9 mmol, 37.5%) of colourless oil.
FTIR (neat, capillary) 2955.56, 1754.65, 1648.64, 1456.39, 1414.83, 1388.75, 1298.51, 1239.97, 1178.60, 1154.64, 1082.23, 1061.84, 1043.84, 1026.67, 943.56, 918.45, 856.41, 832.97, 784.30, 767.03, 694.35, 663.60. NMR ($CDCl_3$) 6.80-7.13 (1H,m), 4.42-4.91 (2H,m), 4.03-4.40 (2H,m), 0.87-1.15 (2H,m), 0.00 (9H,S).



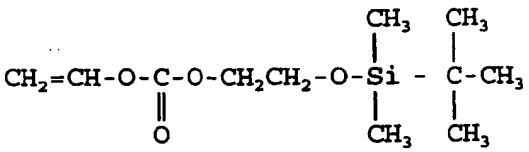
3.2 3-(Trimethylsilyl)propyl Vinyl Carbonate $C_9H_{18}O_3Si$

To a 500 mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, thermometer, and dropping funnel was added 25.0 g (189 mmol) of trimethylsilyl-3-propanol, 16.45 g (208 mmol) of pyridine and 175 mL of toluene. In one portion, 22.1 g (208 mmol) of vinylchloroformate was added to the reaction mixture. An exotherm to 73°C was noted. The mixture was stirred for 3 hours at room temperature then at 50°C for 2 hours then at room temperature for 18 hours. The organic phase was washed with 250 mL 2N HCl then with 250 mL 2N $NaOH_3$ and the organic phase dried with magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil distilled to give a colourless oil (bp 115°C, 35 Torr), 14.7 g (7.27 mmol, 38.5%). FTIR (neat, capillary) 2955.00, 2898.21, 1758.60, 1649.23, 1468.16, 1453.00, 1439.73, 1414.72, 1391.72, 1350.50, 1298.51, 1239.70, 1190.91, 1157.19, 1090.25, 1057.10, 1031.32, 995.02, 944.19, 902.70, 856.58, 833.86, 782.42, 753.39, 691.98. NMR ($CDCl_3$) δ 6.86-7.18 (1H,m), 4.36-4.88 (2H,m), 3.96-4.18 (2H,m), 1.40-1.91 (2H,m), 0.36-0.65 (2H,m), 0.00 (9H,S).



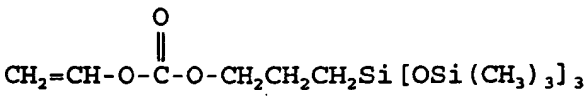
3.3 t-Butyldimethylsiloxyethyl Vinyl Carbonate $C_{11}H_{22}O_4Si$

To a 500 mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, thermometer, dropping funnel, and ice-water bath was added 19.8 g (112.3 mmol) of tert-butyldimethylsiloxy ethyleneglycol, 9.8 g (112.3 mmol) of pyridine and 300 mL of ether. After cooling to 10°C ± 5°C, 11.9 g (112.3 mmol) of vinyl chloroformate was added dropwise so that the temperature was maintained. A precipitate was formed and the reaction was stirred to room temperature over 16 hours. The organic phase was washed twice with 100 mL 2NHCl, twice with 100 mL 2N NaOH then dried over magnesium sulfate. The solvent was flashed off on a rotary evaporator and the resulting oil was passed through a short chromatography column (silica gel, chloroform) to give 26.9 g (109.2 mmol, 97.2%) of clear liquid. FTIR (neat, capillary) 2955.19, 2929.89, 2857.80, 1759.76, 1651.09, 1743.16, 1463.41, 1386.69, 1373.24, 1362.91, 1339.85, 1298.68, 1239.45, 1159.95, 1136.18, 1110.98, 1084.87, 1026.06, 1005.69, 944.16, 902.24, 869.65, 828.32, 812.16, 774.36, 714.82, 682.03, 661.17. NMR ($CDCl_3$) δ 6.78-7.12 91H,m), 4.35-4.93 (2H,m), 4.03-4.26 (2H,m), 3.60-3.83 (2H,m) 0.82 (9H,S), 0.00 (6H,S).



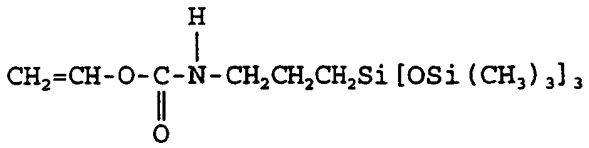
3.4 3-[Tris(trimethylsiloxy)silyl] propyl Vinyl Carbonate $C_{15}H_{36}O_6Si_4$

To a 100 mL 3-neck round bottom flask fitted with a magnetic stirrer, dropping funnel, thermometer, and condenser, was added 9.5 g (38.0 mmol) of 3-(trimethoxysilyl) propyl vinylcarbonate and 16.6 g (125.3 mmol) of trimethylsilylacetate. To this reaction mixture was added 3.45 ml of a catalyst prepared by mixing 23.8 g (242.7 mmol) of sulfuric acid, 11.6 g (251.8 mmol) of absolute ethanol and 16.5 g (916.0 mmol) of water. The addition took twenty minutes and an 8°C exotherm was noted. The reaction was allowed to stir at room temperature for 16 hours and was then diluted with 200 mL of chloroform, washed twice with 100 mL 2N NaOH, and dried over magnesium sulfate. The solvent was removed on a rotary evaporator to give 15.3 g of crude oil. Following chromatography (silica gel, 80% Heptane, 20% methylene chloride) the oil was distilled (bp 125°C, 0.8 Torr), 3.5 g (8.24 mmol, 21.7%). FTIR (neat, capillary) 2958.06, 2898.76, 1762.06, 1650.84, 1543.76, 1393.82, 1319.20, 1298.62, 1245.44, 1199.11, 1160.19, 1041.77, 975.14, 946.32, 833.42, 782.42, 753.08, 714.62, 686.73, 658.57. NMR ($CDCl_3$) 6.71-7.10 (1H,m), 4.28-4.83 (2H,m), 3.85-4.08 (2H,m), 1.36-1.85 (2H,m), 0.23-0.50 (2H,m), 0.00 (27H,S).



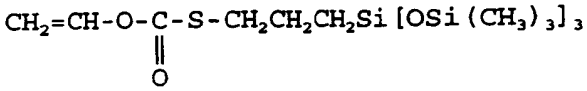
3.5 3-[Tris(trimethylsiloxy)silyl]propyl Vinyl Carbamate $C_{15}H_{17}NO_5Si_4$

To a 100 mL 3-neck round bottom flask fitted with a magnetic stirrer, and dropping funnel was added 5.0 g (14.1 mmol) of 3-amino propyl(trimethylsiloxy)silane, 1.23 g (15.6 mmol) of pyridine and 50 mL of chloroform. Five minutes after adding 1.5 g (14.1 mmol) of vinyl chloroformate, an exotherm resulted. The reaction mixture was checked by gas chromatography after 10 minutes and the starting amine was consumed. The organic phase was washed once with 100 mL 2N HCl then dried with magnesium sulfate. The solvent was removed on a rotary evaporator to afford 5.8 g of crude brown oil. Following chromatography (silica gel, 50% heptane 40% methylenechloride), 5.0 g (11.8 mmol, 83.3%) of colourless oil (bp 130°C, .8 Torr) was obtained. FTIR (neat, capillary) 2957.80, 1751.43, 1718.38, 1648.64, 1529.69, 1445.45, 1407.29, 1293.71, 1249.76, 1195.93, 1165.08, 1041.17, 972.34, 951.33, 833.18, 752.97, 715.26, 686.34, 656.45. NMR ($CDCl_3$) 6.91-7.26 (1H,m), 4.16-4.66 (3H,m), 2.80-3.20 (2H,m), 1.20-1.71 (2H,m), 0.20-0.48 (2H,m), 0.00 (27H,S).



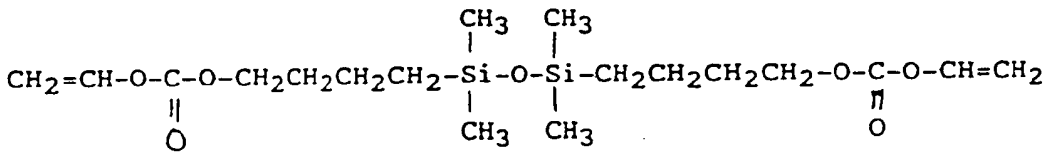
3.6 3-(Vinyloxycarbonylthio)propyl-[tris(trimethylsiloxy)silane]

To a 500 mL 1-neck round bottom flask fitted with a magnetic stirrer and a condenser, was added 33.0 g (123.9 mmol) of 3-(trimethoxysilyl) propyl thio vinyl carbonate and 81.9 g (619.2 mmol) of trimethyl silyacetate. With rapid stirring, 11.3 mL of an acid catalyst prepared by mixing 23.8 g (242.7 mmol) of sulfuric acid, 11.6 g (251.8 mmol) of absolute ethanol and 16.5 g (916.0 mmol) of water unsaturated. A vigorous exotherm was noted. After 30 minutes the reaction mixture was dissolved in 300 mL chloroform and washed twice with 100 mL of 2N NaOH and dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil was chromatographed (silica gel, chloroform). The product was distilled (160°C, .8 Torr) to afford 25.5 g (57.86 mmol, 46.7%) of a colourless oil. FTIR (neat, capillary) 2957.71, 1720.75, 1645.91, 1250.16, 1136.24, 1113.53, 1098.48, 1038.97, 944.04, 912.93, 833.12, 751.61, 717.00, 686.49, 658.44. NMR ($CDCl_3$ δ 6.95-7.32 (1H,m), 4.32=4.85 (2H,m), 2.63-2.88 (2H,m), 1.62-1.88 (2H,m), 0.28-0.62 (2H,m), 0.00 (27,S).



3.7 1,3-Bis[4-(vinyloxycarbonyloxy)but-1-yl]-tetramethyl disiloxane

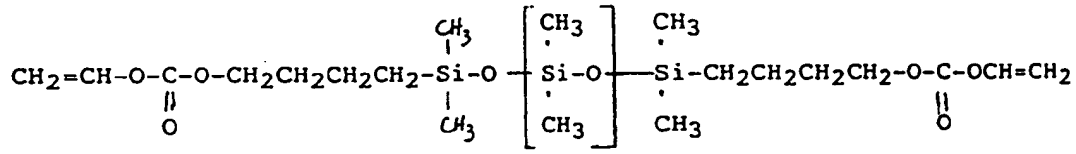
To a 500mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, N_2 blanket, dropping funnel, and thermometer, was added 10.0g (35.9mmol) of 1,3-bis (4-hydroxylbutyl) tetramethylsiloxane, 6.24g (78.9mmol) of pyridine and 100mL of chloroform. Next, 7.64g (71.8mmol) of vinyl chloroformate was added to the mixture dropwise producing an exotherm to 54°C. The reaction mixture was cooled to room temperature and stirred for 19 hours. The organic phase was washed twice with 100mL 2N HCl, twice with 100mL 2N NaOH, then dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil was chromatographed (silica gel, chloroform) to give 13.22g (31.6mmol, 88.1%) of a light yellow oil. FTIR (neat, capillary) 2955.52, 1756.77, 1650.72, 1456.32, 1394.01, 1296.50, 1237.62, 1185.46, 1157.25, 1043.91, 990.80, 944.43, 868.86, 836.27, 781.65, 701.78. NMR ($CDCl_3$) δ 6.80-7.13 (2H,m), 4.37-4.92 (4H,m), 4.00-4.20 (4H,m), 1.55-1.88 (8H,m), 0.33-0.60 (4H,m), 0.00 (12H,S).



3.8 "V_2D_{25}"

To a 100mL 1-neck round bottom microware flask fitted with a magnetic stirrer, and a drying tube was added 5.0g (11.95mmol) of 1,3-bis(4-vinyl butyl carbonate) tetramethyldisiloxane, 22.15g (74.7mmol) of octamethylcyclotetrasiloxane was added. Then 0.679g (0.452mmol) of trifluoromethanesulfonic acid was added to the reaction mixture. The reddish reaction mixture was stirred for 24 hours, then .38g (4.52mmol) of sodium bicarbonate was added which resulted in foaming. After 24 hours a small amount of black solids formed. The reaction mixture was filtered

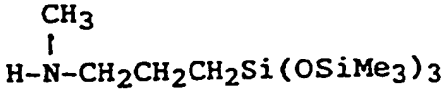
through 20.0g of activated F20 alumina to give a light yellow oil. The oil was heated at 80°C at .25 Torr for 3 1/2 hours to remove volatiles, giving 13.4g (5.90mmol, 49.4%) of a light yellow oil. FTIR (neat, capillary) 2960.92, 1763.97, 1255.70, 1219.52, 1160.33, 1008.42, 946.68, 864.60, 782.03, 700.22, 686.57, 661.36. NMR ($CDCl_3$) δ 6.83-7.16 (2H,m), 4.36-4.93 (4H,m), 4.00-4.20 (4H,m), 1.16-1.91 (8H,m), .32-.62 (4H,m), 0.000 (168,S).



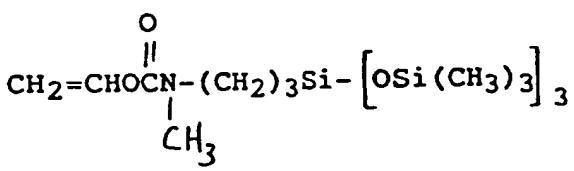
25

3.9 -Methyl-N-[Tris(trimethylsiloxy)silylpropyl] vinyl carbamate

To a 300mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, dropping funnel was added 514.2g (3.186mmols) of hexamethyldisilazane. To the reaction flask was added 675mL of methanol over 30 minutes, when the addition was finished 75.0g (318.6mmol) of N-methyl-3-aminopropyltris(trimethoxy) silane was added. To the reaction was added 57.3g (3.186mmols) of distilled water. The reaction was stirred for 21 days and monitored by GC. During the 21 days 60.0g (3.33mmols) of water, 340mL methanol, and 228.0g (1.41mmols) of hexamethyldisilazane were added. The reaction mixture was reduced to 125.76g of crude oil by rotary evaporation. The crude material was distilled to give 62.6g (169.2mmol, 53.1%) of liquid N-methyl-3-amino-propyltris(trimethylsiloxy)silane bp. 64' 0.125mm Hg. FTIR (neat, capillary) 2957.80, 2899.02, 2790.57, 2361.73, 1471.38, 1443.26, 1412.16, 1343.04, 1249.97, 1218.84, 1187.71, 1083.76, 833.11, 751.60, 715.03, 686.34, 658.34. NMR ($CDCl_3$) 2.20-2.52 (2H,t), 2.24 (3H,s), 1.13-1.66 (2H,m), 0.99 (1H,s), 0.21-0.66 (2H,m), 0.00 (27H,s).



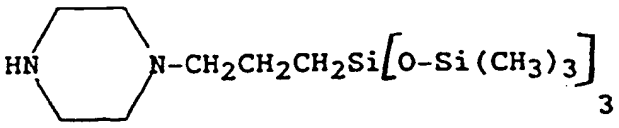
To a 500mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, dropping funnel, thermometer, ice-water bath was added 10.0g (27.2mmol) of N-methyl-3aminopropyltris (trimethylsiloxy) silane, 2.37g (30.0mmol) pyridine, and 200mL ether. Next was added 3.19g (30.0mmol) vinyl chloroformate so that the temperature remained below 15°C. After stirring for 18 hours the reaction mixture was washed with 100mL, 2N HCl and 100mL 2N NaOH, and the organic phase was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil was chromatographed (silica gel, methylene chloride). The product was recovered as an oil and was distilled (94-98°C, .1mm Hg) to yield 8.0g (18.3mmol, 67.2% yield). FTIR (neat, capillary) 2957.78, 2900.92, 1646.60, 1461.07, 1453.17, 1424.97, 1404.46, 1376.48, 1345.30, 1308.70, 1290.62, 1250.02, 1180.15, 1151.93, 1097.66, 1039.05, 952.11, 928.39, 833.42, 787.00, 753.10, 715.30. NMR (2H,t), 2.78 (3H,s), 1.20-1.70 (2H,m), 0.14-0.41 (2H,m), 0.00 (27H,s).



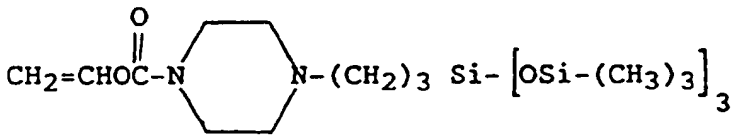
3.10 N-Vinyloxycarbonyl-N'-[tris(trimethylsiloxy)silylpropyl] piperazine

To a 500mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, dropping funnel,

thermometer, oil bath was added 5.0g (58.0mmol) of piperazine and 230mL o-xylene. The reaction mixture was heated to 125 ± 5° and 11.0g (29.0mmol) of 3-chloropropyltris(trimethylsiloxy) silane was added dropwise. The reaction was heated for 48 hours, cooled, and dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil was distilled to give the product 4.5g (10.7mmol, 18.4% yield). FTIR (neat, capillary) 3272.01, 2955.61, 2900.63, 2805.76, 2764.47, 2363.11, 1445.48, 1411.45, 1368.66, 1342.63, 1319.87, 1249.85, 1188.87, 1144.26, 1039.34, 833.42, 751.53, 712.61, 686.39, 656.40. NMR ($CDCl_3$) 3.60-3.93 (4H,m), 2.06-2.43 (6H,m), 1.66 (1H,s), 0.97-1.66 (2H,m), 0.12-0.40 (2H,m), 0.00 (27H,s).

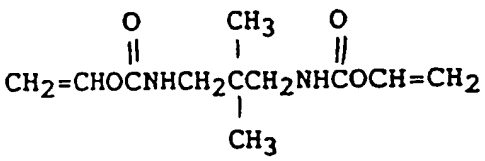


To a 250mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, dropping funnel, thermometer and ice-water bath was added 5.0g (11.8mmol) of 3-tris(trimethylsiloxy)silylpropyl piperazine, .98g (12.4mmol) pyridine and 100mL ether. To the reaction mixture was added 1.32g (12.4mmol) vinyl chloroformate so that the temperature remained below 15°. After stirring for 18 hours the reaction mixture was washed with 100mL 2N HCl, 100mL 2N NaOH and the organic phase was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil was chromatographed (silica gel, methylene chloride). The product was recovered as an oil 4.0g (8.1mmol, 68.8% yield). FTIR (neat, capillary) 2957.40, 2900.69, 2808.30, 2770.50, 1646.32, 1460.48, 1429.87, 1373.46, 1353.45, 1334.61, 1291.27, 1249.73, 1227.01, 1187.92, 1152.02, 1100.89, 1039.50, 1000.33, 952.03, 833.45, 752.98, 712.79, 686.52, 656.44. NMR ($CDCl_3$) 6.89-7.30 (1H,dd), 4.28-4.76 (2H,m), 3.30-3.60 (2H,m), 2.19-2.40 (2H,m), 1.21-1.63 (2H,m), 0.17-0.63 (2H,m), 0.00 (27H,s).



3.11 2,2-Dimethyl N,N-bis(vinyloxycarbonyl)-1,3-propandiamine $C_{11}H_{18}N_2O_4$

To a 250mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, thermometer, nitrogen blanket, dropping funnel, and ice-water bath was added 15.5g (196.0mmol) of pyridine, 100mL of chloroform, 10.0g (98.0mmol) of 2,2-dimethyl-1,3-diamino propane. After cooling to 12.5°C ± 2.5°C, 20.8g (196.0mmol) of vinyl chloroformate was added so that the temperature was maintained. When the addition was completed, the reaction was stirred at room temperature for one hour. The organic phase was washed twice with 100mL 2N HCl, once with distilled water, twice with 2N NaOH, once with distilled water, once with 100mL 2N HCl, once with distilled water then was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting solid was chromatographed (silica gel, ethyl acetate) to afford a white solid (mp 92-98°C), 14.4g (59.5mmol, 60.7%). FTIR 3356.25, 3330.18, 3101.77, 3091.71, 3047.38, 2967.99, 2962.39, 2932.08, 2875.70, 1733.54, 1725.58, 1710.82, 1676.99, 1649.18, 1527.92, 1473.90, 1458.90, 1440.71, 1394.41, 1371.29, 1360.72, 1299.03, 1257.64, 1244.48, 1201.55, 1157.95, 1106.46, 1062.40, 1025.93, 998.01, 979.97, 961.45, 951.57, 876.82, 866.36, 774.00, 720.42, 671.33. NMR ($CDCl_3$) 6.93-7.27 (2H,m), 5.46-5.93 (2H,s), 4.428-4.86 (4H,m), 2.83-3.10 (4H,d), 0.90 (6H,s).



3.12 N-(2-ethyl vinyl carbonate)-3-aminopropyltris(trimethylsiloxy) silane

To a 250mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, dropping funnel, oil bath, thermometer was added 104.3g (1021.0mmol) 2,2-dimethyl-1,3-diaminopropane, 29.3g (79.0mmol) of 3-chloropropyltris (trimethylsiloxy) silane. The reaction was heated at 120°C for 3 hours and stirred to room temperature for 24 hours. The reaction mixture was washed with 100mL 2N NaOH then the organics were dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil distilled to give 23.8g (54.3mmol, 68.6% yield) bp 100°C. FTIR (neat, capillary) 2955.72, 2807.97, 2361.44, 1614.95, 1463.73, 1409.81, 1362.71, 1249.98, 1185.85, 1039.44, 833.64, 753.04, 714.78, 686.41, 657.85. NMR ($CDCl_3$) 2.25-2.56 (6H,m), 1.19-1.63 (2H,m), 1.06 (3H,s), 0.78 (6H,s), 0.07-0.45 (2H,m), 0.00 (27H,s).

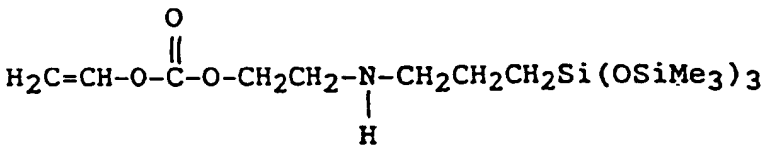
To a 250mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, dropping funnel, ice-water bath, thermometer was added 6.3g (15.8mmol) N-(2-hydroxyethyl)-3-aminopropyltris(trimethylsiloxy) silane, 1.37g (17.4mmol) of pyridine, 100mL ether. To the reaction mixture was added 1.68g (15.8mmol) of vinyl chrloroformate so that the temperature remained below 5°C.

After stirring to room temperature for 24 hours the reaction mixture was washed with 100mL 2N HCl then 100mL 2N NaOH then the organics were dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil, 4.3g, chromatographed (silica gel, ethyl acetate 20% methylene chloride 80%). The oil recovered weighed 2.99g (6.4mmol, 25.4% yield). FTIR (neat, capillary) 2957.62, 2899.00, 1720.60, 1702.33, 1648.16 1470.55, 1420.23, 1373.91, 1291.12, 1249.88, 1196.62, 1152.74, 1039.27, 951.52, 833.44, 753.18, 715.26, 686.53, 658.78. NMR ($CDCl_3$) 6.85-7.20 (1H,dd), 4.20-4.69 (2H,m), 3.36-3.71 (2H,bd), 3.00-3.36 (4H,m), 1.00-1.65 (2H,m), 0.09-0.40 (2H,m), 0.00 (27H,s).

3.13 3-[Tris(trimethylsiloxy)silyl]propylaminoethyl vinyl carbonate

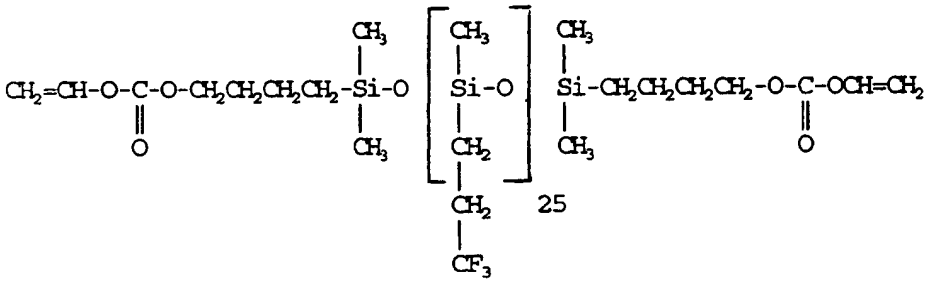
To a 500mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, oil bath and thermometer was added 100mL ethanolamine, 20.0g (53.5mmol) of 3-chloropropyltris (trimethylsiloxy) silane. The reaction was heated at 120°C for 4 hours then at 140°C for 1 hour. The reaction was cooled then diluted with 400mL distilled water then extracted twice with 100mL ether. The combined organics were dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil, 23.0g, chromatographed (silica gel, gradient from 98.75% CH_2Cl_2, 1.25% EtOAc to 100% MeOH) to give 6.6g (16.6mmol, 31.1%) FTIR (neat, capillary) 2957.55, 2898.62, 2834.28, 1453.19, 1411.46, 1249.92, 1191.11, 1039.00, 833.12, 751.49, 714.58, 686.18, 657.92. NMR ($CDCl_3$) 3.09-3.68 (4H,m), 2.25-2.43 (4H,m), 1.17-1.71 (2H,m), 0.07-0.47 (2H,m), 0.00 (27H,s).

To a 250mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, dropping funnel, ice-water bath and thermometer was added 6.3g (15.8mmol) N-(2-hydroxyethyl)-3-aminopropyltris(trimethylsiloxy) silane, 1.37g (17.4mmol) of pyridine and 100mL ether. To the reaction mixture was added 1.68g (15.8mmol) of vinyl chloroformate so that the temperature remained below 5°C. After stirring at room temperature for 24 hours the reaction mixture was washed with 100mL 2N HCl, 100mL 2N NaOH and the organic phase was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil, 4.3g, chromatographed (silica gel, ethyl acetate 20% methylene chloride 80%). The oil recovered weighed 2.99g (6.4mmol, 25.4% yield). FTIR (neat, capillary) 2957.62, 2899.00, 1720.60, 1702.33, 1648.16, 1470.55, 1420.23, 1373.91, 1291.12, 1249.88, 1196.62, 1152.74, 1039.27, 951.52, 833.44, 753.18, 715.26, 686.53, 658.78. NMR ($CDCl_3$) 6.85-7.20 (1H,dd), 4.20-4.69 (2H,m), 3.36-3.71 (2H,bd), 3.00-3.36 (4H,m), 1.00-1.65 (2H,m), 0.09-0.40 (2H,m), 0.00 (27H,s).



3.14 V_2DF_{25}

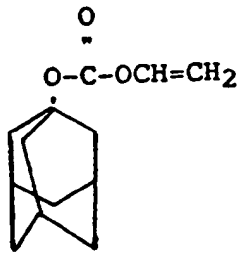
To a 100 mL one neck round bottom flask fitted with a magnetic stirrer, and a drying tube was added 5.0 g (11.95 mmol) of 1,3-bis (4-vinylbutylcarbonate) tetramethyldisiloxane, and 46.6 g (99.6 mmol) of 1,3,5-methyl,1,3,5-trifluoropropylcyclotrisiloxane. To the reaction mixture was added 0.0679 g (0.452 mmol) of trifluoromethanesulfonic acid. The mixture was stirred at room temperature for 24 hours then 0.38 g (4.52 mmol) of sodium bicarbonate was added, and the mixture was allowed to stir an additional 24 hours. The reaction mixture was filtered through 20.0 g of activated F20 alumina to give a light yellow oil. The crude product was vacuum stripped at 90°C 0.025 Torr for 4 hours to give the desired product.



PART IV - SYNTHESIS OF ADAMANTYL MOIETY-CONTAINING MONOMERS

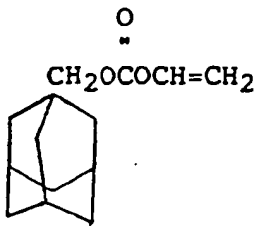
4.0 1-Adamantane vinyl carbonate

To a 500 mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, dropping funnel, ice-saltwater bath and thermometer was added 17.6 g (116.0 mmol) of 1-adamantanol, 9.3 g (117.0 mmol) of pyridine and 200 mL chloroform. To the reactin mixture was added 12.5 g (117.0 mmol) of vinyl chloroformate so that the temperature remained below 10 degrees centigrade. After stirring at room temperature for 18 hours the reaction mixture was washed with 100 mL 2N HCl and 100 mL 2N NaOH and the organic phase was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting white solid chromatographed (silica gel, chloroform). The white solid recovered 19.3 g (86.4 mmol, 74.5% yield) melting point 35-37 degrees centigrade. FTIR (KBr) 3430.92, 2914.51, 2855.03, 1756.33, 1651.33 1458.19, 1321.61, 1312.23, 1296.45, 1246.83, 1160.25, 1103.75, 1082.53, 1041.68, 964.82, 892.90, 784.44. NMR ($CDCl_3$ 6.81-7.20 (1H,dd), 4.33-4.96 (2H,m), 1.50-2.40 (15H,m)



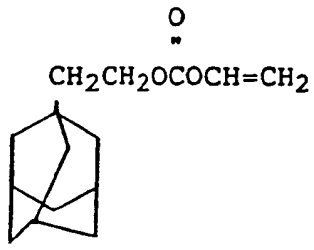
4.1 1-Adamantanemethyl Vinyl Carbonate

To a 500mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, dropping funnel, ice-saltwater bath and thermometer was added 10.0g (60.0mmol) of 1-adamantanmethanol, 4.8g (60.0mmol) of pyridine and 150mL chloroform. To the reaction mixture was added 6.4g (60.0mmol) of vinyl chloroformate so that the temperature remained below 10°C. After stirring at room temperature for 18 hours the reaction mixture was washed with 100mL 2N HCl and 100mL 2 N NaOH and the organic phase was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting solid chromatographed (silica gel, chloroform). The white solid recovered totaled 12.0 (50.8mmol, 84.5% yield), melting point 44-45°C. FTIR (KBr) 3423.04, 2906.49, 2580.27, 1759.74, 1649.15, 1391.84, 1322.44, 1260.77, 1231.42, 1190.53, 1147.22, 1087.78, 982.05, 951.64, 938.71, 889.75. NMR ($CDCl_3$) 6.89-7.27 (1H,dd), 4.40-5.05 (2H,m), 3.75 (2H,s), 1.43-2.13 (15H,m)



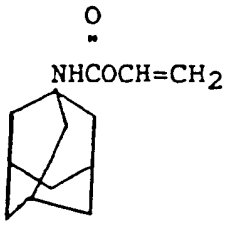
4.2 1-Adamantane Vinyl Carbonate)]

To a 500mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, dropping funnel, ice-saltwater bath, thermometer was added 5.0g (27.7mmol) of 1-adamanthanethanol, 2.2g (27.7mmol) of pyridine and 150mL chloroform. To the reaction mixture was added 2.95g (28.0mmol) of vinyl chloroformate so that the temperature remained below 10 degrees centigrade. After stirring at room temperature for 18 hours the reaction mixture was washed with 100mL 2N HCl and 100mL 2 N NaOH and the organic phase dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil chromatographed (silica gel, chloroform). The oil recovered totaled 27.6g (10.8mmol, 38.5% yield). FTIR (neat, capillary) 2898.57, 2846.95, 1756.14, 1648.61, 1450.70, 1398.71, 1312.71, 1296.74, 1240.05, 1155.26, 1106,22, 1097.88, 1090.63, 975.27, 944.26, 933.77, 923.00, 900.75, 867.0, 782.34. NMR ($CDCl_3$) 6.86-7.20 (1H,dd), 4.38-4.92 (2H,m), 4.072-4.37 (2H,t), 1.33-2.18 (17H,m).



4.3 1-Adamantane Vinyl Carbamate

To a 500mL 3-neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, dropping funnel, ice-saltwater bath and thermometer was added 10.0g (66.0mmol) of 1-adamantaneamine, 5.5g (70.0mmol) of pyridine and 150mL chloroform. To the reaction mixture was added 7.4g (70.0mmol) of vinyl chloroformate so that the temperature remained below 10°C. After stirring at room temperature for 18 hours the reaction mixture was washed with 100mL 2N HCl and 100mL 2 N NaOH and the organic phase was dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting solid was chromatographed (silica gel, chloroform). The tan solid totaled 5.2g (23.5mmol, 35.6% yield). FTIR (KBr) 3435.97, 3341.23, 2919.85, 2906.82, 2852.95, 1738.71, 1718.23, 1648.31, 1522.76, 1362.95, 1347.11, 1296.03, 1280.55, 1229.09, 1188.08, 1173.23, 1131.46, 1054.34, 1044.05, 952.14, 849.30. NMR ($CDCl_3$) 6.94-7.33 (1H,dd), 4.25-4.88 (3H,m), 1.56-2.26 (15H,m).



4.4 N-(2-adamantyl)-0-2-Vinyloxycarbonylaminoethyl Carbamate

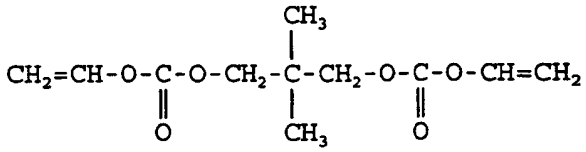
To a 250mL 3-neck round bottom flask that was fitted with a magnetic stirrer, condenser, nitrogen blanket, was added 6.33g (41.8mmol) of 2-adamantamine, 20.7g (41.8mmol) of 20% phosgene in toluene and 90mL of dry toluene. By means of a heating mantle the reaction was refluxed for eight hours, then allowed to cool to room temperature over night. To the reaction mixture was added 5.0g (38.0mmol) of 2-hydroxyethyl vinyl carbamate in 100mL of dry toluene. The reaction mixture was refluxed for eight hours then cooled to room temperature and the product was filtered and dried to give 5.4g (17.5mmol, 46.1% yield). FTIR (Kbr) 3320.53, 2911.77, 2854.81, 2708.48, 2622.82, 2587.66, 2530.60, 2062.48, 1710.68, 1648.47, 1625.62, 1604.50, 1594.43, 1514.68, 1476.34, 1453.03, 1403.83, 1363.71, 1348.91, 1323.96, 1311.36, 1295.64, 1250.12, 1185.17, 1111.58, 1056.19, 1012.80, 974.49, 949.05, 913.42, 863.76, 810.32, 769.55, 730.73, 694.94, 649.43. NMR ($CDCl_3$) 8.54-7.54 (2H,bs), 7.33-6.96 (1H,q), 4.85-4.26 (2H,m), 3.79-3.20 (4H,m), 2.33-1.33 (15H,m).

PART V - SYNTHESIS OF ALKYLENE BRIDGED CROSSLINKERS

5.0 2,2-Dimethyl-1,3-bis-(Vinyloxycarbonyloxy)propane

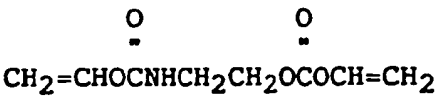
To a 500 mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, thermometer, ice-water bath, and dropping funnel was added 20.0 g (192.0 mmol) of 2,2-dimethyl-1,3-propaneidiol, 16.7 g (211.2 mmol) of pyridine and 200 mL of chloroform. To the reaction mixture was added 20.45 g (192.0 mmol) of vinyl chloroformate was added over 20 minutes. After 1 hour, the reaction was allowed to warm to room temperature for 20 hours. The organic phase was washed twice with 100 mL 2N HCl, twice with 100 mL 2N NaOH and then dried over magnesium sulfate. The solvent was removed on a rotary evaporator to afford an oil. Following chromatography (silica gel, 80% heptane, 20% methylene chloride) 6.4 g (26.2 mmol, 13.6%) of colorless oil was obtained. FTIR (neat, capillary)

2970.57, 1754.14, 1650.67, 1566.446, 1540.34, 1476.77, 1406.71, 1386.46, 1375.68, 1299.22, 1227.23, 1152.73, 1085.68, 1054.54, 1020.91, 961.81, 941.38, 871.66, 779.08, 696.42. NMR ($CDCl_3$ γ 6.80-7.18 (1H,m), 4.45-4.98 (2H,m), 3.98 (4H,S), 1.04 (6H,S).



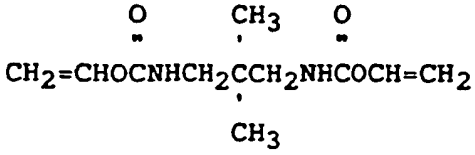
5.1 N,O-bis-(Vinyloxycarbonyl)ethanolamine $C_8H_{11}O_5$

To a 250mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, thermometer, nitrogen blanket, dropping funnel and an ice-water bath was added 27.2g (344.0mmol) of pyridine, 10.0g (164.0mmol) of aminoethanol and 100mL of ether. Next, 36.7g (344.0mmol) of vinyl chloroformate was added so that the temperature remained below 15°C. The reaction was stirred at room temperature for 72 hours and 50mL acetonitrile and 5.0g (50.0mmol) of vinyl chloroformate were added. The mixture was stirred 24 hours and the organic phase washed thrice with 100mL 2N HCl, twice with 100mL distilled water, thrice with 100mL 2N NaOH, twice with 100mL distilled water, once with 100mL 2N HCl, once with 100mL distilled water and then dried with magnesium sulfate. The solvent was removed on a rotary evaporator to give a solid which was chromatographed (silica gel, $CHCl_3$) recrystallized (toluene: heptane, 2:8) to afford a white solid (mp 45-46°C), 9.4g (46.7mmol, 27.2%). FTIR (KBr) 3507.66, 3318.44, 3124.82, 3047.20, 2998.82, 2967.94, 2952.25, 2849.60, 2754.60, 1761.20, 1734.02, 1707.59, 1679,14, 1650.91, 1540.99, 1465.42, 1433.12, 1399.05, 1383.81, 1368.76, 1306.65, 1275.59, 1173.28, 1156.81, 1116.49, 1088.57, 1033.54, 1008.11, 964.70, 948.83, 928.54, 902.88, 887.36, 877.39, 850.91, 782.45, 699.45, 699.43. NMR ($CDCl_3$) 6.83-7.32 (1H,m), 5.06-5.43 (1H,S), 4.37-5.06 (2H,m), 4.27-4.36 (2H,m), 3.30-3.70 (2H,m).



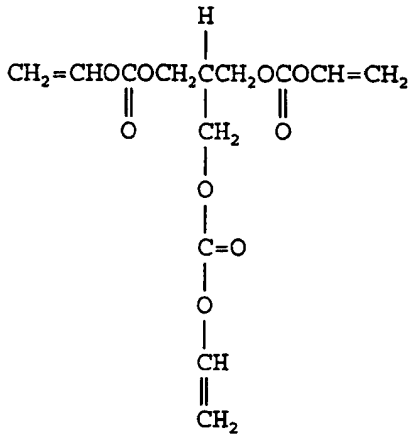
5.2 2,2-Dimethyl-N,N-bis(vinyloxycarbonyl)-1,3-propanediamine $C_{11}H_{18}N_2O_4$

To a 250mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, thermometer, nitrogen blanket, dropping funnel, and ice-water bath was added 15.5g (196.0mmol) of pyridine, 100mL of chloroform and 10.0g (98.0mmol) of 2,2-dimethyl-1,3-diaminopropane. After cooling to 12.5°C ± 2.5°C, 20.8g (196.0mmol) of vinyl chloroformate was added so that the temperature was maintained. When the addition was complete, the reaction was stirred at room temperature one hour. The organic phase was washed twice with 100mL 2N HCl, once with distilled water, twice with 2N NaOH, once with distilled water, once with 100mL 2N HCl, once with distilled water and then dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting solid was chromatographed (silica gel, ethyl acetate) to afford a white solid (mp 92-98°C), 14.4g (59.5mmol, 60.7%). FTIR 3356.25, 3330.18, 3101.77, 3091.71, 3047.38, 2967.99, 2962.39, 2932.08, 2875.70, 1733.54, 1725.58, 1710.82, 1676.99, 1649.18, 1527.92, 1473.90, 1458.90, 1440.71, 1394.41, 1371.29, 1360.72, 1299.03, 1257.64, 1244.48, 1201.55, 1157.95, 1106.46, 1062.40, 1025.93, 998.01, 979.97, 961.45, 951.57, 876.82, 866.36, 774.00, 720.42, 671.33. NMR ($CDCl_3$) 6.93-7.27 (2H,m), 5.46-5.93 (2H,S), 4.428-4.86 (4H,m), 2,83-3.10 (4H,d), 0.90 (6H,S).



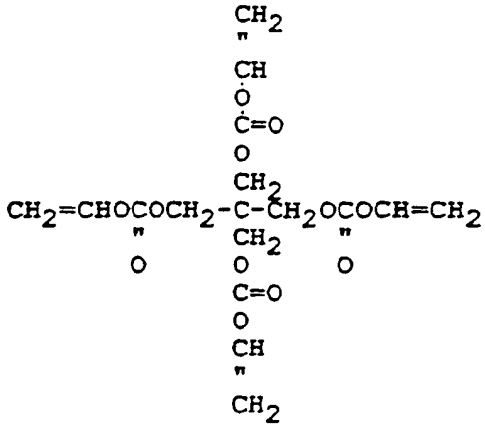
5.3 1,2,3-tris(vinyloxycarbonyloxy)propane

To a 250 mL three neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, and a dropping funnel was added 3.1 g (33.7 mmol) of glycerol, 8.7 g (110 mmol) of pyridine and 125 mL of anhydrous acetonitrile. The reaction flask was cooled in an ice water bath so that the temperature did nto exceed 5°C. To the reaction mixture was added 11.7 g (110 mmol) of vinylchloro formate over 30 minutes. The reaction mixture was allowed to stir to room temperature overnight. The solvent was removed on a rotary evaporator and the crude product was taken up in ethyl acetate and washed with 2 100 mL portions of 2N HCl, then 2 100 mL portions of 2N NaOH, then 2 100 mL portions of brine. The organics were dried with magnesium sulfate, the solvent removed and the crude product distilled to obtain the pure product.



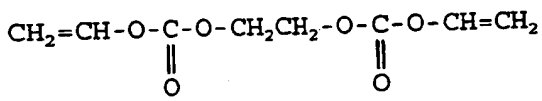
5.4 1,3-bis(vinyloxycarbonyloxy)-2,2-bis(vinyloxy carbonyloxymethyl) propane

To a 250 mL three neck round bottom flask fitted with a mechanical stirrer, condenser, nitrogen blanket, and a dropping funnel was added 3.0 g (22.0 mmol) of pentaerythritol, 7.7 g (97 mmol) of pyridine and 125 mL of anhydrous acetonitrile. The reaction flask was cooled in an ice water bath so that the temperature did not exceed 5°C. To the reaction mixture was added 10.3 g (97 mmol) of vinylchloroformate over 30 minutes. The reaction mixture was allowed to stir to room temperature overnight. The solvent was removed on a rotary evaporator and the crude product was taken up in ethyl acetate and washed with two 100 mL portions of 2N HCl, then two 100 mL portions of 2N NaOH, then two 100 mL portions of brine. The organic phase was dried with magnesium sulfate, the solvent removed and the crude product distilled to obtain the pure product.



5.5 1,2-bis-(Vinyloxycarbonyloxy)ethane

To a 100 mL 3-neck round bottom microware flask fitted with a magnetic stirrer, condenser, N_2 blanket, and dropping funnel was added 5.0 g (81.6 mmol) of ethylene glycol, 12.8 g (163.0 mmol) of pyridine and 50 mL of chloroform. To the reaction mixture, 17.38 g (163.2 mmol) of vinyl chloroformate was added over 5 minutes. The black reaction mixture was stirred at room temperature for 72 hours. The reaction mixture was washed once with 100 mL 2N HCl, once with 100 mL 2N NaOH and then dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting oil chromatographed (silica gel, chloroform). The product was distilled (110°C, 5 Torr) to afford 6.5 g (32.2 mmol, 39.4%) of a colourless oil. FTIR (neat, capillary) 1752.03, 1648.58, 1455.73, 1445.68, 1406.42, 1386.28, 1373.53, 1345.23, 1301.17, 1268.47, 1221.46, 1152.52, 1080.66, 1028.57, 1007.91, 941.86, 903.05, 866.96, 777.05, 696.37. NMR ($CDCl_3$) δ 6.85-7.18 (2H,m), 4.52-5.04 (4H,m), 4.40 (4H,S).



5.6 1,6-divinylhexyldicarbamate

To a 500mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, dropping funnel, thermometer was added 5.0g (43mmol) of 1,6 diaminohexane, 7.12g (90mmol) of pyridine, 100mL anhydrous acetonitrile, 100mL ether. After the starting material was dissolved 9.26g (87mmol) of vinyl chloroformate was added over 20 minutes an exoterm was noted, and a precipitate formed over 18 hours. The solvent was removed on a rotary evaporator and the residue was dissolved in methylene chloride, washed with 2N NaOH, thrice with distilled water then dried with magnesium sulfate. The solid was coated on silica gel and chromatographed (97% CH_2Cl_2, 3% ETOAc) to give a solid that was dissolved in methylene chloride and slowly added to stirred heptane. The solid recovered was dried to give 5.7g (22.2mmol, 51.7% yield) melting point 94-98°C. FTIR 3333.74, 3086.01, 3032.62, 2947.83, 2886.20, 2857.98, 1713.28, 1682.02, 1648.85, 1528.09, 1476.87, 1465.92, 1339.48, 1294.01, 1259.77, 1224.55, 1156.32, 1051.88, 1001.10, 954.5, 875.05, 866.57. NMR ($CDCl_3$) 7.00-7.34 (2H,q) 4.62-5.13 (2H,bs), 4.29-4.75 (4H,m), 2.91-3.33 (4H,q), 1.31 (8H,bs).

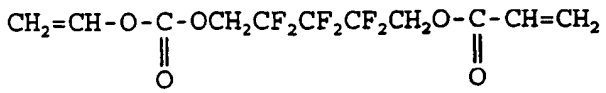
5.7 1,8-divinyloctyldicarbamate

To a 500mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, dropping funnel, thermometer was added 5.0g (34.6mmol) of 1,8 diaminooctane, 6.1g (76.1mmol) of pyridine, 100mL anhydrous acetonitrile, 100mL ether. After the starting material was dissolved 8.0g (87mmol) of vinyl chloroformate was added over 20 minutes an exotherm was noted, and a precipitate formed over 18 hours. The solvent was removed on a rotary evaporator and the residue was dissolved in methylene chloride, washed with 2N NaOH, thrice with distilled water then dried with magnesium sulfate. The solid was coated on silica gel and chromatographed (97% CH_2Cl_2, 3% ETOAc) to give a solid that was dissolved in methylene chloride and slowly added to stirred heptane. The solid recovered was dried to give 6.7g (22.1mmol, 64.1% yield) melting point 83-88°C. FTIR 3336.20, 3086.75, 3032.18, 2996.55, 2942.19, 2926.73, 2872.60, 2855.14, 1709.82, 1676.68, 1649.06, 1530.29, 1478.71, 1464.03, 1362.59, 1308.80, 1257.38, 1252.87, 1213.85, 1168.05, 1083.04, 1062.73, 1031.76, 956.24, 874.73, 861.46. NMR ($CDCl_3$) 6.95-7.34 (2H,q), 4.62-5.13 (2H,bs), 4.29-4.75 (4H,m), 2.97-3.30 (4H,q), 1.31 (10H,bs).

PART VI - FLUOROALKYLENE BRIDGED CROSSLINKERS

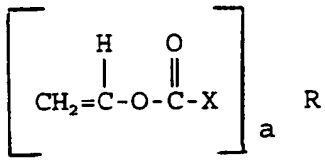
6.0 1,5-bis-(Vinyloxycarbonyloxy)-2,2,3,3,4,4-hexafluoropentane $C_{11}H_{10}F_6O_6$

To a 500 mL 3-neck round bottom flask fitted with a magnetic stirrer, condenser, nitrogen blanket, thermometer, dropping funnel, and ice-water bath was added 12.3 g (155.5 mmol) of pyridine and 200 mL of methylene chloride. After cooling to 5°C ± 2°C add 16.57 g (155.5 mmol) of vinyl chloroformate was added so that the temperature was maintained. A white precipitate formed immediately. When the addition was complete, 15.0 g (70.7 mmol) of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol in one portion as a slurry with 250 mL methylene chloride was added. The reaction was allowed to warm to room temperature for 18 hours. The organics were washed twice with 250 mL of 2N HCl then dried with magnesium sulfate. The solvent was removed on a rotary evaporator to afford 24.7 g of a straw oil. Following chromatography (silica gel, toluene), 21.8 g (61.9 mmol, 87.6%) of colourless oil was obtained. FTIR (neat, capillary) 3102.29, 2983.43, 1767.41, 1651.43, 1442.83, 1404.75, 1303.52, 1247.26, 1151.88, 1125.91, 1095.64, 1031.24, 1005.65, 985.71, 939.37, 882.43, 776.53, 697.20, 673.23, 650.18. NMR ($CDCl_3$) δ 6.83-7.26 (2H,m), 4.30-5.23 (8H,m).



Claims

1. A compound of the general formula:



wherein

a is 1, 2, 3 or 4;

X is -O-, -S- or -NR^3-;

R^3 is H or a monovalent alkyl radical; and

R is selected from an organosilicon radical, a heterocyclic-containing radical, an adamantyl-containing radical, an alkylene radical, a fluoroalkylene radical and a hydroxyalkyl radical.

2. A compound according to Claim 1, wherein R is an organosilicon radical.

3. A compound according to Claim 1, wherein R is a pyrrolidinone-containing radical.

4. A compound according to any preceding claim, wherein X is -NR^3-.

5. A compound according to any one of Claims 1-3, wherein X is -O-.

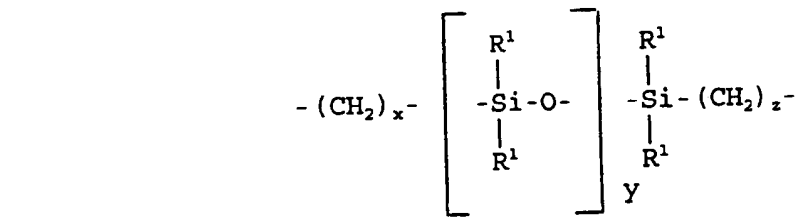
6. A compound according to any one of Claims 1-3, wherein X is -S-.

7. A compound according to Claim 1 which is trimethylsilylmethyl vinyl carbonate, trimethylsilylethyl vinyl carbonate, 3-(trimethylsilyl)propyl vinyl carbonate, t-butyldimethylsiloxyethyl vinyl carbonate, 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbonate, 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbamate, 3-(vinyloxycarbonylthio)propyl-[tris(trimethylsiloxy)silane], N-[tris(trimethylsiloxy)silylpropyl]-N-methyl vinyl carbamate, N-vinyloxycarbonyl-N'-[tris(trimethylsiloxy)silyl]propyl piperazine or 3-[tris(trimethylsiloxy)silyl]propylaminoethyl vinyl carbonate.

8. A compound according to Claim 1 which is N-(vinyloxycarbonyloxyethyl-pyrrolidine-2,5-dione, 3-(2-pyrrolidinone-1-yl)propyl vinyl carbonate, 2,(2-pyrrolidinone-1-yl)propyl vinyl carbonate or 2,(2-pyrrolidinone-1-yl)ethyl vinyl carbonate.

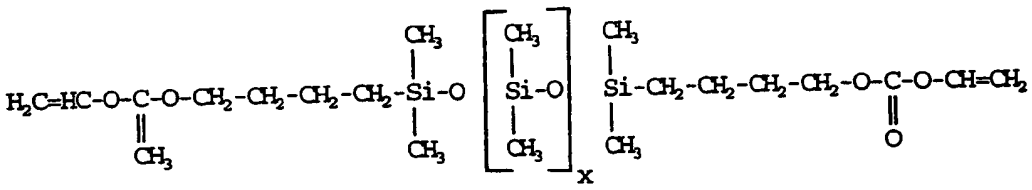
9. A compound according to Claim 1 which is 2-hydroxyethyl vinyl carbonate or 2-hydroxyethyl vinyl carbamate.

10. A compound according to Claim 2, wherein a is 2 and R is of the general formula:



where x and z are 1 to 6, y is on average between 2 and 200, and R^1 is an alkyl radical or a fluorinated alkyl radical.

11. A compound according to Claim 2, having the formula:



where x is on average 25.

12. A compound according to Claim 2 which is 1,3-bis[4-vinyloxycarbonyloxy)but-1-yl]tetramethyl disiloxane or the propargyl vinyl carbamate of 1,3-bis[4-vinyloxycarbonyloxy)but-1-yl]tetramethyl disiloxane.

13. A compound of Claim 1 which is 1,5-bis(vinyloxycarbonyloxy)-2,2,3,3,4,4-hexafluoropentane.

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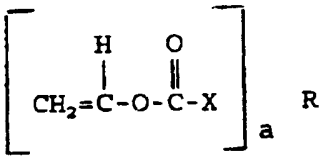
(71) Applicant: **BAUSCH & LOMB INCORPORATED**
Rochester, New York 14604-2701 (US)

(72) Inventors:
- **Bambury, Ronald E.**
  Fairport, New York 14450 (US)
- **Seelye, David E.**
  Rochester, New York 14624 (US)

(74) Representative: **Allam, Peter Clerk**
LLOYD WISE, TREGEAR & CO.,
Commonwealth House,
1-19 New Oxford Street
London WC1A 1LW (GB)

(54) Vinyl carbonate and vinyl carbamate monomers for a contact lens material

(57) There is provided a compound of the general formula:



wherein

a is 1, 2, 3 or 4;
X is -O-, -S- or -NR^3-;
R^3 is H or a monovalent alkyl radical; and
R is selected from an organosilicon radical, a heterocyclic-containing radical, an adamantyl-containing radical, an alkylene radical, a fluoroalkylene radical and a hydroxyalkyl radical.

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2.13.15/3.4

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EUROPEAN SEARCH REPORT

Application Number
EP 96 20 2972

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	FR-A-2 603 886 (SOCIETE NATIONALE DES POUDRES ET EXPLOSIFS) * examples 8,10 *	1,5	C07C69/96 C07C271/00 C07D207/00 C07F7/00
X	JOURNAL OF ORGANIC CHEMISTRY, vol. 53, no. 2, 1988, pages 423-425, XP000615324 M. JUNG ET AL: "Improved synthesis of 3-substituted 7-methoxybenzofurans, useful intermediates for preparation of morphine analogues" * page 424; example 13 *	1	C08F218/00 G02B1/04
X	ANNALI DI CHIMICA, vol. 54, 1964, ROMA, pages 520-520-529, XP002022118 G. MATTALIA ET AL.: "Su alcuni nuovi derivati carbammici dell'1-fenil-2,3-dimetil-pirazolone-5" * p.524, compound 23; p.529, last paragraph *	1	
A	JOURNAL OF POLYMER SCIENCE: PART C, no. 24, 1968, pages 75-88, XP002022119 J. SCHAEFGEN: "Poly(vinyl chloroformate) and derivatives: preparation and properties" * page 86 - page 88 *	1	
A	US-A-2 532 011 (C. DAHLQUIST ET AL.) * column 7, line 42 - column 8, line 10 *	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
C07C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	6 January 1997	Glikman, J-F

CATEGORY OF CITED DOCUMENTS

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